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(54) Title: COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

(57) Abstract: The invention relates to a method of bleaching a substrate that comprises applying to the substrate, in an aqueous medium, a specified ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen. Also provided is an aqueous bleaching composition substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. Also provided is a method of treating a textile such as a laundry fabric whereby a complex catalyses bleaching of the textile by atmospheric oxygen after the treatment. The catalyst may be used in dry form, or in a liquor that is then dried, such as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid.

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COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

FIELD OF INVENTION

This invention relates to compositions and methods for
5 catalytically bleaching substrates with atmospheric oxygen,
more particularly using a defined class of ligand or complex
as catalyst. This invention also relates to a method of
treating textiles, such as laundry fabrics, using the
defined class of ligand or complex as catalyst, more
10 specifically to a method whereby bleaching by atmospheric
oxygen is catalysed after the treatment.

BACKGROUND OF INVENTION

Peroxygen bleaches are well known for their ability to
15 remove stains from substrates. Traditionally, the substrate
is subjected to hydrogen peroxide, or to substances which
can generate hydroperoxyl radicals, such as inorganic or
organic peroxides. Generally, these systems must be
activated. One method of activation is to employ wash
20 temperatures of 60°C or higher. However, these high
temperatures often lead to inefficient cleaning, and can
also cause premature damage to the substrate.

A preferred approach to generating hydroperoxyl bleach
25 radicals is the use of inorganic peroxides coupled with
organic precursor compounds. These systems are employed for
many commercial laundry powders. For example, various
European systems are based on tetraacetyl ethylenediamine
(TAED) as the organic precursor coupled with sodium
30 perborate or sodium percarbonate, whereas in the United
States laundry bleach products are typically based on sodium

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nonanoyloxybenzenesulfonate (SNOBS) as the organic precursor coupled with sodium perborate.

Precursor systems are generally effective but still exhibit 5 several disadvantages. For example, organic precursors are moderately sophisticated molecules requiring multi-step manufacturing processes resulting in high capital costs. Also, precursor systems have large formulation space requirements so that a significant proportion of a laundry 10 powder must be devoted to the bleach components, leaving less room for other active ingredients and complicating the development of concentrated powders. Moreover, precursor systems do not bleach very efficiently in countries where consumers have wash habits entailing low dosage, short wash 15 times, cold temperatures and low wash liquor to substrate ratios.

Alternatively, or additionally, hydrogen peroxide and peroxy systems can be activated by bleach catalysts, such as by 20 complexes of iron and the ligand N4Py (i.e. N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) disclosed in WO95/34628, or the ligand Tpen (i.e. N, N, N', N'-tetra(pyridin-2-yl-methyl)ethylenediamine) disclosed in WO97/48787. According to these publications, molecular 25 oxygen may be used as the oxidant as an alternative to peroxide generating systems. However, no role in catalysing bleaching by atmospheric oxygen in an aqueous medium is reported.

30 It has long been thought desirable to be able to use atmospheric oxygen (air) as the source for a bleaching

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species, as this would avoid the need for costly hydroperoxyl generating systems. Unfortunately, air as such is kinetically inert towards bleaching substrates and exhibits no bleaching ability. Recently some progress has 5 been made in this area. For example, WO 97/38074 reports the use of air for oxidising stains on fabrics by bubbling air through an aqueous solution containing an aldehyde and a radical initiator. A broad range of aliphatic, aromatic and heterocyclic aldehydes is reported to be useful,

10 particularly para-substituted aldehydes such as 4-methyl-, 4-ethyl- and 4-isopropyl benzaldehyde, whereas the range of initiators disclosed includes N-hydroxysuccinimide, various peroxides and transition metal coordination complexes.

15 However, although this system employs molecular oxygen from the air, the aldehyde component and radical initiators such as peroxides are consumed during the bleaching process. These components must therefore be included in the composition in relatively high amounts so as not to become 20 depleted before completion of the bleaching process in the wash cycle. Moreover, the spent components represent a waste of resources as they can no longer participate in the bleaching process.

25 Accordingly, it would be desirable to be able to provide a bleaching system based on atmospheric oxygen or air that does not rely primarily on hydrogen peroxide or a hydroperoxyl generating system, and that does not require the presence of organic components such as aldehydes that 30 are consumed in the process. Moreover, it would be

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desirable to provide such a bleaching system that is effective in aqueous medium.

- It may also be noted that the known art teaches a bleaching effect only as long as the substrate is being subjected to the bleaching treatment. Thus, there is no expectation that hydrogen peroxide or peroxy bleach systems could continue to provide a bleaching effect on a treated substrate, such as a laundry fabric after washing and drying, since the bleaching species themselves or any activators necessary for the bleaching systems would be assumed to be removed from the substrate, or consumed or deactivated, on completing the wash cycle and drying.
- 15 It would be therefore also be desirable to be able to treat a textile such that, after the treatment is completed, a bleaching effect is observed on the textile. Furthermore, it would be desirable to be able to provide a bleach treatment for textiles such as laundry fabrics whereby 20 residual bleaching occurs when the treated fabric has been treated and is dry.

SUMMARY OF INVENTION

- We have found that a selected class of ligand or complex is 25 surprisingly effective in catalysing the bleaching of substrates using atmospheric oxygen or air. Furthermore, we have found certain novel ligands which are useful in the bleaching of substrates using atmospheric oxygen or air.
- 30 Accordingly, in a first aspect, the present invention provides a bleaching composition comprising, in an aqueous

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medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing bleaching of a substrate by the atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. The medium is therefore preferably insensitive or stable to catalase, which acts on peroxy species.

In a second aspect, the present invention provides a method 10 of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen.

15 Furthermore, in a third aspect, the present invention provides the use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach 20 system, the complex catalysing bleaching of the substrate by the atmospheric oxygen.

We have also found that certain ligands or complexes of this class are surprisingly effective in catalysing bleaching of 25 the substrate by atmospheric oxygen after treatment of the substrate.

Accordingly, in a fourth aspect, the present invention provides a method of treating a textile by contacting the 30 textile with a ligand which forms a complex with a

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transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment.

In a fifth aspect, the present invention provides a dry
5 textile having a ligand as defined above applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

Advantageously, the method according to the present
10 invention permits all or the majority of the bleaching species in the medium (on an equivalent weight basis) to be derived from atmospheric oxygen. Thus, the medium can be made wholly or substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. Furthermore, the
15 complex is a catalyst for the bleaching process and, as such, is not consumed but can continue to participate in the bleaching process. The catalytically activated bleaching system of the type in accordance with the present invention, which is based on atmospheric oxygen, is therefore both
20 cost-effective and environmentally friendly. Moreover, the bleaching system is operable under unfavourable wash conditions which include low temperatures, short contact times and low dosage requirements. Furthermore, the method is effective in an aqueous medium and is therefore
25 particularly applicable to bleaching of laundry fabrics. Therefore, whilst the composition and method according to the present invention may be used for bleaching any suitable substrate, the preferred substrate is a laundry fabric. The bleaching method may be carried out by simply leaving the
30 substrate in contact with the medium for a sufficient period

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of time. Preferably, however, the aqueous medium on or containing the substrate is agitated.

- An advantage of the method according to the fourth aspect of
5 the invention is that, by enabling a bleaching effect even after the textile has been treated, the benefits of bleaching can be prolonged on the textile. Furthermore, since a bleaching effect is conferred to the textile after the treatment, the treatment itself, such as a laundry wash
10 cycle, may for example be shortened. Moreover, since a bleaching effect is achieved by atmospheric oxygen after treatment of the textile, hydrogen peroxide or peroxy-based bleach systems can be omitted from the treatment substance.
- 15 The present invention also extends to a commercial package comprising a bleaching composition comprising a ligand or complex as defined below together with instructions for its use.
- 20 The present invention also extends to use of a ligand or complex as defined below in the manufacture of a bleaching composition, the bleaching composition substantially devoid of peroxygen bleach or a peroxy-based or peroxy-generating bleach system.
- 25
- DETAILED DESCRIPTION OF THE INVENTION
- The ligand may be present as a preformed complex of a ligand and a transition metal. Alternatively, the composition may comprise a free ligand that complexes with a transition
30 metal already present in the water or that complexes with a transition metal present in the substrate. The composition

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may also be formulated as a composition of a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal, whereby the complex is formed *in situ* in the medium.

5

The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, 10 cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

The ligand forms a complex of the general formula (A1):

15



in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V) and W(IV)-(V)-(VI), preferably selected from Fe(II)-(III)-(IV)-(V);

L represents a ligand as herein defined, or its protonated or deprotonated analogue;

25 X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner, preferably selected from O^{2-} , RBO_2^{2-} , $RCOO^-$, $RCONR^-$, OH^- , NO_3^- , NO , S^{2-} , RS^- , PO_4^{3-} , PO_3OR^{3-} , H_2O , CO_3^{2-} , HCO_3^- , ROH , 30 $N(R)_3$, ROO^- , O_2^{2-} , O_2^- , RCN , Cl^- , Br^- , OCN^- , SCN^- , CN^- , N_3^- , F^- , I^- , RO^- , ClO_4^- , and $CF_3SO_3^-$, and more preferably selected from

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O^{2-} , RBO_2^{2-} , $RCOO^-$, OH^- , NO_3^- , S^{2-} , RS^- , PO_3^{4-} , H_2O , CO_3^{2-} , HCO_3^- , ROH , $N(R)_3$, Cl^- , Br^- , OCN^- , SCN^- , RCN , N_3^- , F^- , I^- , RO^- , ClO_4^- , and $CF_3SO_3^-$;

Y represents any non-coordinated counter ion,
5 preferably selected from ClO_4^- , BR_4^- , $[MX_4]^-$, $[MX_4]^{2-}$, PF_6^- , $RCOO^-$, NO_3^- , RO^- , $N^+(R)_4$, ROO^- , O_2^{2-} , O_2^- , Cl^- , Br^- , F^- , I^- , $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^- , SCN^- , H_2O , RBO_2^{2-} , BF_4^- and BPh_4^- , and
more preferably selected from ClO_4^- , BR_4^- , $[FeCl_4]^-$, PF_6^- ,
10 $RCOO^-$, NO_3^- , RO^- , $N^+(R)_4$, Cl^- , Br^- , F^- , I^- , $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^- , SCN^- , H_2O and BF_4^- ;

a represents an integer from 1 to 10, preferably from 1 to 4;

k represents an integer from 1 to 10;

n represents an integer from 1 to 10, preferably from 1 to 4;

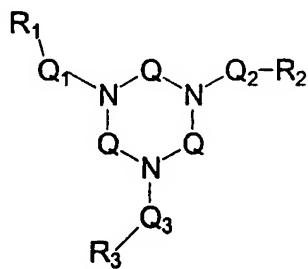
m represents zero or an integer from 1 to 20, preferably from 1 to 8; and

each R independently represents a group selected from hydrogen, hydroxyl, -R' and -OR', wherein R'= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R' being optionally substituted by one or more functional groups E, wherein E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR', -NH₂, -NHR', -N(R')₂, -N(R')₃⁺, -C(O)R', -OC(O)R', -COOH, -COO⁻ (Na⁺, K⁺), -COOR', -C(O)NH₂, -C(O)NHR', -C(O)N(R')₂, heteroaryl, -R', -SR', -SH, -P(R')₂, -P(O)(R')₂, -P(O)(OH)₂, -P(O)(OR')₂, -NO₂, -SO₃H, -SO₃⁻(Na⁺, K⁺), -S(O)₂R', -NHC(O)R', and -N(R')C(O)R', wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, -NH₃⁺, -SO₃H, -SO₃⁻(Na⁺, K⁺), -COOH, -COO⁻(Na⁺, K⁺), -

- 10 -

$\text{P}(\text{O})(\text{OH})_2$, or $-\text{P}(\text{O})(\text{O}^-(\text{Na}^+, \text{K}^+))_2$, and preferably each R independently represents hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C_{1-4} -alkyl.

The ligand L is of the general formula (I):



10

(I)

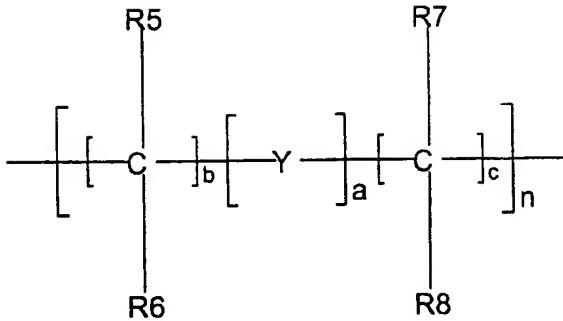
wherein

15 R_1 , R_2 , and R_3 independently represent a group selected from hydrogen, hydroxyl, halogen, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$, $-\text{R}$ and $-\text{OR}$, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E;

20 Q independently represent a group selected from C_{2-3} -alkylene optionally substituted by H, benzyl or C_{1-8} -alkyl;

Q_1 , Q_2 and Q_3 independently represent a group of the formula:

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wherein

5 $5 \geq a+b+c \geq 1$; $a=0-5$; $b=0-5$; $c=0-5$; $n=1$ or 2 ;

Y independently represents a group selected from $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(O)-$, arylene, alkylene, heteroarylene, heterocycloalkylene, $-(G)P-$, $-P(O)-$ and $-(G)N-$, wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E; and

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, $-R$ and $-OR$, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E, or R5 together with R6, or R7 together with R8, or both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C_{1-6} -alkylene optionally substituted by C_{1-4} -alkyl, $-F$, $-Cl$, $-Br$ or $-I$,

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provided that at least one, preferably at least two, of R₁, R₂ and R₃ is a coordinating group.

At least two, and preferably at least three, of R₁, R₂ and R₃ independently represent a group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, 10 quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. Preferably, at least two of R₁, R₂, R₃ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted 15 imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

Preferably, substituents for groups R₁, R₂, R₃, when representing a heterocyclic or heteroaromatic ring, are 20 selected from C₁₋₄-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

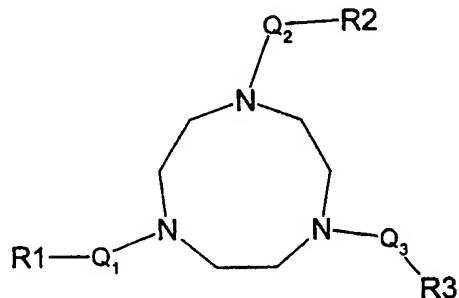
The groups R5, R6, R7, R8 preferably independently represent 25 a group selected from -H, hydroxy-C₀-C₂₀-alkyl, halo-C₀-C₂₀-alkyl, nitroso, formyl-C₀-C₂₀-alkyl, carboxyl-C₀-C₂₀-alkyl and esters and salts thereof, carbamoyl-C₀-C₂₀-alkyl, sulfo-C₀-C₂₀-alkyl and esters and salts thereof, sulfamoyl-C₀-C₂₀-alkyl, amino-C₀-C₂₀-alkyl, aryl-C₀-C₂₀-alkyl, C₀-C₂₀-alkyl, 30 alkoxy-C₀-C₆-alkyl, carbonyl-C₀-C₆-alkoxy, and C₀-C₂₀-alkylamide. Preferably, none of R6-R8 is linked together.

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Preferably, Q_1 , Q_2 and Q_3 are defined such that $a=b=0$,
 $c=1, 2, 3$ or 4 and $n=1$. Preferably, the groups Q_1 , Q_2 and Q_3
independently represent a group selected from $-\text{CH}_2-$ and -
5 CH_2CH_2- .

Group Q is preferably a group selected from $-\text{CH}_2\text{CH}_2-$ and -
 $\text{CH}_2\text{CH}_2\text{CH}_2-$.

10 In a first preferred embodiment, the ligand L is of the
general formula (II):



15 wherein R_1 , R_2 , R_3 are as defined previously for R_1 , R_2 , R_3 ,
and Q_1 , Q_2 , Q_3 are as defined previously.

Preferred classes of ligands according to the first
preferred embodiment, as represented by formula (II) above,
20 are as follows:

(i) ligands of the general formula (II) wherein:
R1, R2, R3 each independently represent a coordinating
group selected from carboxylate, amido, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$,
25 hydroxyphenyl, an optionally substituted heterocyclic ring

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or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and
5 thiazole.

In this class, we prefer that:

R1, R2, R3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl,
10 optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

(ii) ligands of the general formula (II) wherein:

15 two of R1, R2, R3 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine,
20 pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

one of R1, R2, R3 represents a group selected from hydrogen, C₁₋₂₀ optionally substituted alkyl, C₁₋₂₀ optionally substituted arylalkyl, aryl, and C₁₋₂₀ optionally substituted NR₃⁺ (wherein R=C₁₋₈-alkyl).

In this class, we prefer that:

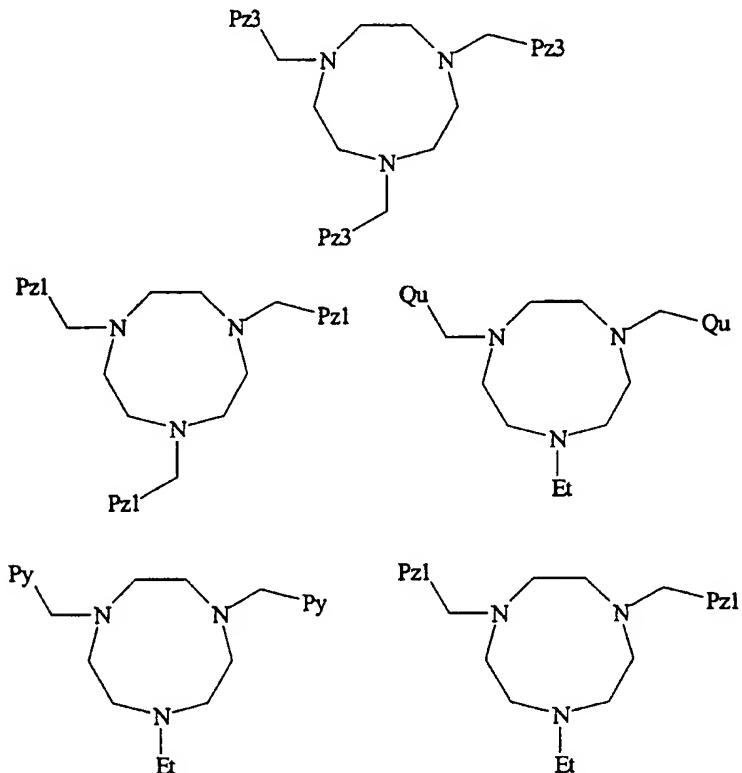
two of R1, R2, R3 each independently represent a
30 coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl,

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optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and
 one of R1, R2, R3 represents a group selected from
 hydrogen, C₁₋₁₀ optionally substituted alkyl, C₁₋₅-furanyl, C₁₋₅
 5 optionally substituted benzylalkyl, benzyl, C₁₋₅ optionally
 substituted alkoxy, and C₁₋₂₀ optionally substituted N⁺Me₃.

In especially preferred embodiments, the ligand L is
 selected from:

10



wherein -Et represents ethyl, -Py represents pyridin-2-yl,
 Pz3 represents pyrazol-3-yl, Pz1 represents pyrazol-1-yl,
 15 and Qu represents quinolin-2-yl.

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- The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as RCOO^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , RSO_4^- , SO_4^{2-} ,
5 NO_3^- , F^- , Cl^- , Br^- , or I^- , with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.
- 10 Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from $\text{R}'\text{COO}^-$, ClO_4^- , BF_4^- , PF_6^- , RSO_3^- (in particular CF_3SO_3^-), RSO_4^- , SO_4^{2-} ,
15 NO_3^- , F^- , Cl^- , Br^- , and I^- , wherein R represents hydrogen or optionally substituted phenyl, naphthyl or $\text{C}_1\text{-C}_4$ alkyl.

It will be appreciated that the complex (A1) can be formed by any appropriate means, including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A1) under conditions of storage or use. Preferably, the complex is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as FeSO_4 can be mixed in solution with the ligand L, or a

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ligand L-generating species, to form the active complex. Thus, for example, the composition may be formed from a mixture of the ligand L and a metal salt MX_n in which preferably $n=1-5$, more preferably 1-3. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according to the formula (A1).

The bleaching compositions according to the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.). As is generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

In the context of the present invention bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with a substrate. However, it is envisaged that the present invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate. Furthermore, in the

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context of the present invention bleaching is to be understood as being restricted to any bleaching mechanism or process that does not require the presence of light or activation by light. Thus, photobleaching compositions and processes relying on the use of photobleach catalysts or photobleach activators and the presence of light are excluded from the present invention.

In typical washing compositions the level of the catalyst is such that the in-use level is from $1\mu\text{M}$ to 50mM , with preferred in-use levels for domestic laundry operations falling in the range 10 to $100 \mu\text{M}$. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching.

Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

The bleaching composition of the present invention has particular application in detergent formulations, especially for laundry cleaning. Accordingly, in another preferred embodiment, the present invention provides a detergent bleach composition comprising a bleaching composition as defined above and additionally a surface-active material, optionally together with detergency builder.

The bleach composition according to the present invention may for example contain a surface-active material in an amount of from 10 to 50% by weight. The surface-active

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material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available
5 and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulfates and sulfonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl groups. Examples of suitable synthetic anionic detergent compounds are sodium
15 and ammonium alkyl sulfates, especially those obtained by sulfating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{20}) benzene sulfonates, particularly sodium linear secondary alkyl ($C_{10}-C_{15}$) benzene sulfonates; sodium alkyl glyceryl
20 ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium and ammonium salts of sulfuric acid esters of higher (C_9-C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide,
25 reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulfonates such as those derived by reacting alpha-
30 olefins (C_8-C_{20}) with sodium bisulfite and those derived by reacting paraffins with SO_2 and Cl_2 , and then hydrolysing with

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- a base to produce a random sulfonate; sodium and ammonium (C₇-C₁₂) dialkyl sulfosuccinates; and olefin sulfonates, which term is used to describe material made by reacting olefins, particularly (C₁₀-C₂₀) alpha-olefins, with SO₃ and 5 then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C₁₀-C₁₅) alkylbenzene sulfonates, and sodium (C₁₆-C₁₈) alkyl ether sulfates.
- 10 Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C₆-C₂₂) phenols, generally 5-25 EO, i.e. 5-25 units of 15 ethylene oxides per molecule; and the condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine 20 oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not 25 normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

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The detergent bleach composition of the invention will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is
5 free from C₁₆-C₁₂ fatty acid soaps.

The bleach composition of the present invention may also contain a detergency builder, for example in an amount of from about 5 to 80 % by weight, preferably from about 10 to
10 60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

15 Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy
20 succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

25 Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or
30 amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known

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as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

In particular, the compositions of the invention may contain
5 any one of the organic and inorganic builder materials,
though, for environmental reasons, phosphate builders are
preferably omitted or only used in very small amounts.
Typical builders usable in the present invention are, for
example, sodium carbonate, calcite/carbonate, the sodium
10 salt of nitrilotriacetic acid, sodium citrate,
carboxymethoxy malonate, carboxymethoxy succinate and
water-insoluble crystalline or amorphous aluminosilicate
builder materials, each of which can be used as the main
builder, either alone or in admixture with minor amounts of
15 other builders or polymers as co-builder.

It is preferred that the composition contains not more than
5% by weight of a carbonate builder, expressed as sodium
carbonate, more preferably not more than 2.5 % by weight to
20 substantially nil, if the composition pH lies in the lower
alkaline region of up to 10.

Apart from the components already mentioned, the bleach
composition of the present invention can contain any of the
25 conventional additives in amounts of which such materials
are normally employed in fabric washing detergent
compositions. Examples of these additives include buffers
such as carbonates, lather boosters, such as alkanolamides,
particularly the monoethanol amides derived from palmkernel
30 fatty acids and coconut fatty acids; lather depressants,
such as alkyl phosphates and silicones; anti-redeposition

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agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulfate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

10 Transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as EDTMP (ethylene diamine tetra(methylene phosphonate)) may also be included, in addition to the ligand specified, for example to improve the stability sensitive ingredients such as enzymes, fluorescent 15 agents and perfumes, but provided the composition remains bleaching effective. However, the composition according to the present invention containing the ligand, is preferably substantially, and more preferably completely, devoid of transition metal sequestrants (other than the ligand).

20 Whilst the present invention is based on the catalytic bleaching of a substrate by atmospheric oxygen or air, it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in 25 the composition, if desired. Therefore, by "substantially devoid of peroxygen bleach or peroxy-based or -generating bleach systems" is meant that the composition contains from 0 to 50 %, preferably from 0 to 10 %, more preferably from 0 to 5 %, and optimally from 0 to 2 % by molar weight on an 30 oxygen basis, of peroxygen bleach or peroxy-based or -generating bleach systems. Preferably, however, the

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composition will be wholly devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

Thus, at least 10 %, preferably at least 50 % and optimally at 5 least 90 % of any bleaching of the substrate is effected by oxygen sourced from the air.

According to the fourth aspect, the catalyst may be contacted to the textile fabric in any suitable manner. For 10 example, it may be applied in dry form, such as in powder form, or in a liquor that is then dried, for example as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. Other suitable means of contacting 15 the catalyst to the textile may be used, as further explained below.

Any suitable textile that is susceptible to bleaching or one 20 that one might wish to subject to bleaching may be used. Preferably the textile is a laundry fabric or garment.

The bleaching method of the fourth aspect may be carried out by simply leaving the substrate in contact with the catalyst for a sufficient period of time. Preferably, however, the 25 catalyst is in an aqueous medium, and the aqueous medium on or containing the substrate is agitated.

In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated 30 temperatures.

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In a particularly preferred embodiment the method according to the fourth aspect is carried out on a laundry fabric using aqueous treatment liquor. In particular the treatment may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent wash liquor. The catalyst can be delivered into the wash liquor from a powder, granule, pellet, tablet, block, bar or other such solid form. The solid form can comprise a carrier, which can be particulate, sheet-like or comprise a three-dimensional object. The carrier can be dispersible or soluble in the wash liquor or may remain substantially intact. In other embodiments, the catalyst can be delivered into the wash liquor from a paste, gel or liquid concentrate.

It is particularly advantageous that the catalyst used in the method of the fourth aspect makes use of atmospheric oxygen in its bleaching activity. This avoids the requirement that peroxygen bleaches and/or other relatively large quantities of reactive substances need be used in the treatment process. Consequently, only a relatively small quantity of bleach active substance need be employed and this allows dosage routes to be exploited which could previously not be used. Thus, while it is preferable to include the catalyst in a composition that is normally used in a washing process, such as a pre-treatment, main-wash, conditioning composition or ironing aid, other means for ensuring that the catalyst is present in the wash liquor may be envisaged.

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For example, it is envisaged that the catalyst can be presented in the form of a body from which it is slowly released during the whole or part of the laundry process. Such release can occur over the course of a single wash or 5 over the course of a plurality of washes. In the latter case it is envisaged that the catalyst can be released from a carrier substrate used in association with the wash process, e.g. from a body placed in the dispenser drawer of a washing machine, elsewhere in the delivery system or in the drum of 10 the washing machine. When used in the drum of the washing machine the carrier can be freely moving or fixed relative to the drum. Such fixing can be achieved by mechanical means, for example by barbs that interact with the drum wall, or employ other forces, for example a magnetic force. 15 The modification of a washing machine to provide for means to hold and retain such a carrier is envisaged similar means being known from the analogous art of toilet block manufacture. Freely moving carriers such as shuttles for dosage of surfactant materials and/or other detergent 20 ingredients into the wash can comprise means for the release of the catalyst into the wash.

In the alternative, the catalyst can be presented in the form of a wash additive that preferably is soluble. The 25 additive can take any of the physical forms used for wash additives, including powder, granule, pellet, sheet, tablet, block, bar or other such solid form or take the form of a paste, gel or liquid. Dosage of the additive can be unitary or in a quantity determined by the user. While it is 30 envisaged that such additives can be used in the main

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washing cycle, the use of them in the conditioning or drying cycle is not hereby excluded.

The present invention is not limited to those circumstances
5 in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In these circumstances it is envisaged that the catalyst can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement
10 which is being employed, such as a brush, bat or dolly, or from any suitable applicator.

Suitable pre-treatment means for application of the catalyst to the textile material prior to the main wash include
15 sprays, pens, roller-ball devices, bars, soft solid applicator sticks and impregnated cloths or cloths containing microcapsules. Such means are well known in the analogous art of deodorant application and/or in spot treatment of textiles. Similar means for application are
20 employed in those embodiments where the catalyst is applied after the main washing and/or conditioning steps have been performed, e.g. prior to or after ironing or drying of the cloth. For example, the catalyst may be applied using tapes, sheets or sticking plasters coated or impregnated
25 with the substance, or containing microcapsules of the substance. The catalyst may for example be incorporated into a drier sheet so as to be activated or released during a tumble-drier cycle, or the substance can be provided in an impregnated or microcapsule-containing sheet so as to be
30 delivered to the textile when ironed.

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Throughout the description and claims generic groups have been used, for example alkyl, alkoxy, aryl. Unless otherwise specified the following are preferred group restrictions that may be applied to generic groups found
5 within compounds disclosed herein:

alkyl: linear and branched C1-C8-alkyl,

10 alkenyl: C2-C6-alkenyl,

cycloalkyl: C3-C8-cycloalkyl,

alkoxy: C1-C6-alkoxy,

15 alkylene: selected from the group consisting of: methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylidene; 1,2-propylene; 1,3-propylene; 2,2-propylidene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,3-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; cyclopentan-1,2-diyl; and
20 cyclopentan-1,3-diyl,

aryl: selected from homoaromatic compounds having a molecular weight under 300,

25 arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphthalenylene; 1,3-naphthalenylene; 1,4-naphthalenylene; 2,3-naphthalenylene; 1-hydroxy-2,3-phenylene; 1-hydroxy-2,4-phenylene; 1-hydroxy-30 2,5-phenylene; and 1-hydroxy-2,6-phenylene,

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- heteroaryl: selected from the group consisting of:
pyridinyl; pyrimidinyl; pyrazinyl; triazolyl; pyridazinyl;
1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl;
imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl;
- 5 oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl,
wherein the heteroaryl may be connected to the compound via
any atom in the ring of the selected heteroaryl,
- heteroarylene: selected from the group consisting of:
10 pyridindiyl; quinolindiyl; pyrazodiyl; pyrazoldiyl;
triazolediyl; pyrazindiyl; and imidazolediyl, wherein the
heteroarylene acts as a bridge in the compound via any atom
in the ring of the selected heteroarylene, more specifically
preferred are: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-
15 2,5-diyl; pyridin-2,6-diyl; pyridin-3,4-diyl; pyridin-3,5-
diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; quinolin-2,8-
diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-
1,3-diyl; pyrazol-3,5-diyl; triazole-3,5-diyl; triazole-1,3-
diyl; pyrazin-2,5-diyl; and imidazole-2,4-diyl,
- 20 heterocycloalkyl: selected from the group consisting of:
pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl;
piperazinyl; hexamethylene imine; 1,4-piperazinyl;
tetrahydrothiophenyl; tetrahydrofuranyl; 1,4,7-
25 triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl;
1,4,7,10,13-pentaazacyclopentadecanyl; 1,4-diaza-7-thia-
cyclononanyl; 1,4-diaza-7-oxa-cyclononanyl; 1,4,7,10-
tetraazacyclododecanyl; 1,4-dioxanyl; 1,4,7-trithia-
cyclononanyl; tetrahydropyranyl; and oxazolidinyl, wherein
30 the heterocycloalkyl may be connected to the compound via
any atom in the ring of the selected heterocycloalkyl,

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heterocycloalkylene: selected from the group consisting of:
piperidin-1,2-ylene; piperidin-2,6-ylene; piperidin-4,4-
ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene;
5 1,4-piperazin-2,5-ylene; 1,4-piperazin-2,6-ylene; 1,4-
piperazin-1,2-ylene; 1,4-piperazin-1,3-ylene; 1,4-piperazin-
1,4-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-
3,4-ylene; tetrahydrothiophen-2,3-ylene; tetrahydrofuran-
2,5-ylene; tetrahydrofuran-3,4-ylene; tetrahydrofuran-2,3-
10 ylene; pyrrolidin-2,5-ylene; pyrrolidin-3,4-ylene;
pyrrolidin-2,3-ylene; pyrrolidin-1,2-ylene; pyrrolidin-1,3-
ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-
ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-
2,9-ylene; 1,4,7-triazacyclonon-3,8-ylene; 1,4,7-
15 triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-
1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene;
1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-
tetraazacyclotetradec-2,5-ylene; 1,4,8,11-
tetraazacyclotetradec-1,2-ylene; 1,4,8,11-
20 tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-
tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-
1,7-ylene; 1,4,7,10-tetraazacyclododec-1,2-ylene; 1,4,7,10-
tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-
2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene;
25 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4,7,10,13-
pentaazacyclopentadec-2,3-ylene; 1,4,7,10,13-
pentaazacyclopentadec-1,2-ylene; 1,4,7,10,13-
pentaazacyclopentadec-2,2-ylidene; 1,4-diaza-7-thia-
cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-1,2-ylene;
30 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-
cyclonon-6,8-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene;

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1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-1,2-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-diaza-7-oxa-cyclonon-6,8-ylene; 1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,3-ylene; 1,4-dioxan-2,6-ylene;
5 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,3-ylene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; tetrahydropyran-2,2-ylidene; 1,4,7-trithia-cyclonon-2,3-ylene; 1,4,7-trithia-cyclonon-2,9-ylene; and 1,4,7-trithia-cyclonon-2,2-ylidene,

10

amine: the group $-N(R)_2$, wherein each R is independently selected from: hydrogen; C₁-C₆-alkyl; C₁-C₆-alkyl-C₆H₅; and phenyl, wherein when both R are C₁-C₆-alkyl both R together may form an -NC₃ to an -NC₅ heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,
15

halogen: selected from the group consisting of: F; Cl; Br and I,

20

sulfonate: the group $-S(O)_2OR$, wherein R is selected from: hydrogen; C₁-C₆-alkyl; phenyl; C₁-C₆-alkyl-C₆H₅; Li; Na; K; Cs; Mg; and Ca,

25 sulfate: the group $-OS(O)_2OR$, wherein R is selected from: hydrogen; C₁-C₆-alkyl; phenyl; C₁-C₆-alkyl-C₆H₅; Li; Na; K; Cs; Mg; and Ca,

30 sulfone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C₁-C₆-alkyl; phenyl; C₁-C₆-alkyl-C₆H₅ and amine (to give sulfonamide) selected from the group: $-NR'2$,

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wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming
5 an alkyl substituent to the heterocyclic ring,

carboxylate derivative: the group -C(O)OR, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,
10

carbonyl derivative: the group -C(O)R, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give amide) selected from the group: -NR'2, wherein each R' is independently selected from:
15 hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

20 phosphonate: the group -P(O)(OR)2, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphate: the group -OP(O)(OR)2, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,
25

phosphine: the group -P(R)2, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl;
30 and C1-C6-alkyl-C6H5,

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- phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C₁-C₆-alkyl; phenyl; and C₁-C₆-alkyl-C₆H₅; and amine (to give phosphonamidate) selected from the group: -NR'₂, wherein each R' is
5 independently selected from: hydrogen; C₁-C₆-alkyl; C₁-C₆-alkyl-C₆H₅; and phenyl, wherein when both R' are C₁-C₆-alkyl both R' together may form an -NC₃ to an -NC₅ heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.
- 10 Unless otherwise specified the following are more preferred group restrictions that may be applied to groups found within compounds disclosed herein:
- 15 alkyl: linear and branched C₁-C₆-alkyl,
alkenyl: C₃-C₆-alkenyl,
cycloalkyl: C₆-C₈-cycloalkyl,
20 alkoxy: C₁-C₄-alkoxy,
alkylene: selected from the group consisting of: methylene; 1,2-ethylene; 1,3-propylene; butan-2-ol-1,4-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl;
25 cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; and cyclopentan-1,2-diyl,
aryl: selected from group consisting of: phenyl; biphenyl; naphthalenyl; anthracenyl; and phenanthrenyl,

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arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphthalenylene; 1,4-naphthalenylene; 2,3-naphthalenylene and 1-hydroxy-2,6-phenylene,

5

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl, wherein the heteroaryl may be connected to the compound via any atom in
10 the ring of the selected heteroaryl,

heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,6-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl;
15 isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-3,5-diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of: pyrrolidinyl; morpholinyl; piperidinyl; piperidinyl; 1,4-piperazinyl; tetrahydrofuranyl; 1,4,7-triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4,7,10-tetraazacyclododecanyl; and piperazinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the
25 selected heterocycloalkyl,

heterocycloalkylene: selected from the group consisting of: piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,6-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-

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ylene; pyrrolidin-2,5-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-
5 tetraazacyclotetradec-1,8-ylene;
1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene;
1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-
tetraazacyclododec-1,7-ylene;
10 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-
tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-
pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-
pentaazacyclopentadec-1,7-ylene; 1,4-diaza-7-thia-cyclonon-
1,4-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-
15 thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-
ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-diaza-7-oxa-
cyclonon-2,2-ylidene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-
ylidene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-
ylene; and tetrahydropyran-2,2-ylidene,
20
amine: the group -N(R)₂, wherein each R is independently selected from: hydrogen; C₁-C₆-alkyl; and benzyl,

halogen: selected from the group consisting of: F and Cl,
25
sulfonate: the group -S(O)₂OR, wherein R is selected from: hydrogen; C₁-C₆-alkyl; Na; K; Mg; and Ca,

sulfate: the group -OS(O)₂OR, wherein R is selected from:
30 hydrogen; C₁-C₆-alkyl; Na; K; Mg; and Ca,

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sulfone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

5

carboxylate derivative: the group $-C(O)OR$, wherein R is selected from hydrogen; Na; K; Mg; Ca; C1-C6-alkyl; and benzyl,

10 carbonyl derivative: the group: $-C(O)R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

15

phosphonate: the group $-P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

20 phosphate: the group $-OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

25 phosphine: the group $-P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

30 phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'2$, wherein each R' is

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independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

The invention will now be further illustrated by way of the
5 following non-limiting examples:

EXAMPLES

10 The following compounds were prepared and tested for catalytic bleaching activity using air:

Compound 1: $[Fe(L^1)]\{FeCl_4\}Cl$

$L^1=1,4,7\text{-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane}$

15

Compound 2: $[Fe(L^2)]\{FeCl_4\}Cl$

$L^2=1,4,7\text{-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane}$

20 Compound 3: $[FeL^3Br]ClO_4$

$L^3=1,4\text{-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane}$

Compound 4: $[FeL^4Cl](ClO_4)_2$

25 $L^4=1,4\text{-bis(pyridin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane}$

Compound 5: $[FeL^5Br]BPh_4$

30 $L^5=1,4\text{-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane}$

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(Compounds 1 and 2 for these studies were received from Prof. F. Mani, University of Florence, Florence, Italy, hereby gratefully acknowledged).

5 Syntheses:

Synthesis of starting materials:

1,4,7-triazacyclononane

10 Ligand 1,4,7-triazacyclononane was produced according the modified method used by the team of Prof. Wieghardt . In this method the detosylation of the 1,4,7-tris-p-toluenesulfon-1,4,7-triazacyclononanamide is performed in 5 minutes in hot sulphuric acid of 180°C. Once the solution
15 has cooled down it is transferred into ether under vigorous stirring. The solution that surfaces is decanted and the residue is dissolved in some boiling water. At boiling temperature drops of concentrated hydrochloric acid are added. The brown crystals that precipitate are drained off
20 and washed with cold hydrochloric acid and then with ethanol and ether. The 1,4,7-triazacyclononane. trihydrochloride thus produced is then processed further as described by Wieghardt et al (K. Wieghardt et al, Chem Ber., 112, 2200
25 (1979)).

25

1,4,7-triazatricyclo[5.2.1.0^{4|10}]decane (orthoamide)
0.5 mol 1,4,7-triazacyclononane, 64.3 g, 0.54 mol orthoformic acid triethylester, 74.8 g, and 20 mmol p-toluolsulphonacid, 4 g, are heated to 150°C. The ethanol
30 that is created and some of the esters are distilled off. After the reaction has been completed the orthoamide can be

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distilled off at a pressure of <80 mbar in the form of a bright yellow volatile oil (b.p. 350 K at 133 Pa), in agreement with literature (T.J. Atkins, *J. Am. Chem. Soc.*, 102, 6365 (1980)).

5

1-ethyl-1,4,7-triazacyclononane (Et-tacn)

Into a mixture of 0.1 mol orthoamide, 13.92 g, dissolved in dry THF, slowly 0.1 mol ethylbromide, 10.9 g, is dripped.

The suspension is stirred for 2 days at room temperature in
10 a closed flask. The microcrystalline powder is drained off and washed with some dry THF. The resulting bromide salt is very hygroscopic. The salt is dissolved in 80 ml water and boiled for 4 hours under back-flow. Then 16 g sodium hydroxide dissolved in 20 ml water is added. This creates a
15 4 molar reaction mixture. Immediately, a bright yellow oil is separated. To complete the reaction, boiling is continued for another 20 hours. After cooling down 300 ml toluol is added and the water is distilled off by means of a water separator. The reaction mixture is filtered and the toluol
20 is drained off by a rotary evaporator. The remaining product is a bright yellow oil. Yield: 13.8 g (89%). ¹H-NMR (CDCl₃-
270 MHz; 300K): 2.59-2.39 (m; 14H); 1.83 (s, 2H); 0.90 ppm
(t; 3H); ¹³C-NMR: 52.1; 50.7; 46.5; 46.4; 12.4 ppm.

25 Compound 3: [Fe(1,4-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane)Br] (ClO₄):

Quinolin-2-ylmethylbromide

The quinolinemethylbromide is produced as follows. In this
30 method 0.2 mol quinoline (30.0 g) with 0.22 mol N-bromsuccinimid (42 g) and dibenzoylperoxide as starter are

- 40 -

placed in 300 ml freshly distilled benzene under irradiation of light. The succinimid that is sedimented after strong cooling is filtered off and the benzene is rotated off. The remaining oil is put into 5% hydrobromic acid. Under cooling 5 with ice a saturated solution of sodiumcarbonate is added to the watery solution up to a pH-value of 7. The precipitated yellowish product is drained off and recrystallized from pentane.

10 *1,4-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane (L³)*

20 mmol Et-tacn (3.12 g) is dissolved in 50 ml dry THF and diluted with 8 ml triethylamine (56.8 mmol). Then 40 mmol quinolin-2ylmethylbromide (8.96 g) is added, after which the 15 solution turns brown. The reaction mixture is stirred for 3 days. The resulting triethylammoniumbromide is filtered off and the THF is rotated off. What remains is a red to brown oil. The by-products (approx. 8%) created by the alkaline hydrolysis of the chinolylmethylbromide could not be 20 separated by HPLC, GC or chromatography, the ligand analysed.

Yield: 6.6 g (75%). ¹H-NMR (CDCl₃, 400 MHz; 300K): 7.92 (d;2H); 7.89 (d;2H); 7.62 (d;2H); 7.52 (d;2H); 7.50 (m;2H); 7.34 (m;2H); 3.87 (s;4H); 2.94 (m;4H); 2.88 (m;4H); 2.68 (m;4H); 2.53 (q;2H); 0.92 ppm (t; 3H); ¹³C-NMR: 160.2; 147.1; 135.9; 129.0; 128.5; 127.2; 127.0; 125.8; 121.1; 64.9; 55.3; 54.3; 53.6; 51.1; 11.8 ppm. MS (EI): 439 (M⁺; rel int 20%); 157 (rel int. 40% - quinoline-2carboxaldehyde); 143 (rel int 100%-quinoline).

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[Fe(1,4-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane)Br] (ClO₄):

Dissolve 1 mmol 1,4-bis(quinolin-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane, 0.44 g, in 30 ml methanol (bright yellow)
5 and lead through argon. Add 1 mmol FeBr₂ (0.22) g. Heat the reaction mixture for 2 hours under back-flow and argon atmosphere. An orange solution is produced. The solution is filtered via an argon frit under protective gas atmosphere to remove undissolved iron bromide. Sodium perchlorate is
10 added to the filtrate and stirred for 2 hours at room temperature. An orange solid is produced. This can be drained off quickly by air and washed with ether. The product is air-stable.

Yield: 400 mg (59%). Elem. Anal. Found: C: 48.24; H: 4.63;
15 N: 10.02%. Calc.: C: 49.85; H: 4.89; N: 10.38%

Compound 4: [Fe(1,4-bis(pyridyl-2-methyl)-7-ethyl-1,4,7-triazacyclononane)Cl] (ClO₄)₂:

20 1,4-bis(pyridyl-2-methyl)-7-ethyl-1,4,7-triazacyclononane (L⁴)
7.76 g Et-tacn (50 mmol) is suspended in 120 ml water, then 16.4 g picolylhydrochloride (100 mmol) is added, after which the solution turns yellow. Under cooling with ice 8.0 g NaOH
25 is added in portions over a period of 5 days in such a way that the pH-value remains below 9 and the temperature does not exceed 0°C. The solution gradually becomes red to brown. The solution is put in the refrigerator for one day. Any organic phase that has formed is separated. The watery phase
30 is extracted by repeated shaking with chloroform. The combined organic phases are dried over CaO. The chloroform

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is rotated off and a thick, mostly red-brown oil remains. This oil is still contaminated by traces of picolylchloride and by-products of the alkaline hydrolysis of the picolylchlorides (approx. 5%). A further purification 5 without analysis of the ligand L⁴ by HPLC, GC or chromatography was not possible. Yield: 14.3 g (84%)
¹H-NMR (CDCl₃, - 400 MHz; 300K): 8.34 (d; 2H); 7.47 (m; 2H); 7.31 (d; 2H); 6.97 (m; 2H); 3.68 (s; 4H); 2.78 (m; 4H); 2.73 (m; 4H); 2.67 (m; 4H); 2.49 (q; 2H); 0.90 ppm (t; 3H); ¹³C-
10 NMR: 159.8; 145.6; 140.0; 123.0; 121.5; 63.8; 55.8; 55.0;
54.3; 51.7; 12.2 ppm. MS (EI): m/z: 339.

[FeL²Cl] (ClO₄)₂

The iron complex was prepared in analogous manner to the
15 formation of the complex for Compound 3.

Compound 5: [Fe(1,4-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane)Br] (BPh₄) :

20 1,4-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane
(L⁵)
The ligand can be synthesised by heating 20 mmol Et-tacn
(3.10 g), 40 mmol pyrazolylmethanol (3.92) (ref W. Driessens,
Recl. Trav., Chim. Pays-Bas, 101, 441, 1982) and 0.4 g LiOH
25 in 50 ml acetonitrile for 20 hours under back-flow and argon
atmosphere. The solution is filtered and the solvent is
rotated off. The product has the form of a bright yellow
oil. Yield: 6.3 g (80%). ¹H-NMR (CDCl₃, - 400 MHz; 300K): 7.43
(d; 4H); 6.21 (s; 2H); 4.93 (s, 4H); 2.83 (m; 8H); 2.62 (m;
30 4H); 2.53 (q; 2H); 0.95 (t, 3H); ¹³C-NMR: 139.0; 129.3;

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125.9; 72.6; 54.3; 53.5; 52.7; 51.7; 12.3 ppm. MS (EI): m/z: 317.

[Fe(1,4-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane)Br] (BPh₄):
5 mmol FeBr₂, 0.22 g, is dissolved in oxygen-free ethanol under boiling. 1 mmol 1,4-bis(pyrazol-1-ylmethyl)-7-ethyl-1,4,7-triazacyclononane (0.32 g) is dissolved in 30 ml ethanol (bright yellow) and led through Ar. The ligand
10 solution is then added in drops. After one hour sodium tetraphenylborate in oxygen-free acetone is added in drops and immediately a bright solid is formed. This is stirred for approx. another 2 hours in an argon atmosphere. The solid is quickly drained off in air and washed repeatedly
15 with ether. The white solid is air-stable. Yield: 480 mg (62%). Elel. Anal. Found: C: 61.95; H: 6.80; N: 12.48%.
Calc.: C: 62.18; H: 6.09; N: 12.70%

20 Ligand L⁶: 1,4-bis(3,5-dimethylpyrazol-1-ylmethyl)-7-ethyl-
1,4,7-triazacyclononane:

This ligand can be produced by heating 3.10 g Et-tacn (20 mmol), 5.13 g 3,5-dimethylpyrazol-1-ylmethanol (40 mmol) (ref W. Driesssen, Recl. Trav., Chim. Pays-Bas, 101, 441, 1982) and 0.5 g potassium carbonate in 50 ml acetonitrile under back-flow and argon atmosphere. The solution is filtered and the solvent is rotated off. The product has the form of a bright yellow oil.
25 Yield: 3.7 g (50%). ¹H-NMR (CDCl₃- 400 MHz; 300K): 5.72 (s; 2H); 4.69 (s, 4H); 2.78 (m; 8H); 2.58 (m; 4H); 2.46 (q; 2H);
30

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2.20 (s; 6H); 2.13 (s; 6H); 0.93 (t, 3H); ^{13}C -NMR: 147.0; 139.2; 105.3; 69.6; 54.5; 53.5; 53.0; 51.7; 13.4; 12.6; 11.2 ppm. MS (EI): m/z: 373.

5 Ligand L⁷: 1,4-bis(1-methylimidazol-2-ylmethyl)-7-ethyl-
1,4,7-triazacyclononane:

1-methylimidazolyl-1-methanol

The 1-methylimidazolyl-1-methanol is produced according to a modified literature procedure (R.C. Jones, J. Am. Chem. Soc., 10 71, 383 (1949)). In this method 41.05 g 1-methylimidazol (0.5 mol) and 15.15 g paraformaldehyde (0.5 mol) are heated together in an autoclave for 24 hours at 140°C, during which a pressure of approx. 10 bar develops. The autoclave is 15 allowed to cool down to approx. 90°C and then opened. The reaction mixture is poured into a flask and the autoclave is rinsed with methanol. The methanol is rotated off and the residue is put in ethanol. Next, 75 ml concentrated HCl is added. The reaction mixture is reduced to dry matter. A 20 sticky brown residue remains, that is dissolved in ethanol preferably boiling as little as possible. After some cooling down 400 ml ether is added quickly. A beige-white substance is produced, which is sticky after draining off. The product is dried for several weeks over P₂O₅.

25

2-chloromethyl-1-methyl-imidazolhydrochloride

The 2-chloromethyl-1-methyl-imidazolhydrochloride is produced according to the description above. 20 ml thionylchloride is added to a suspension of 5.61 g 1- 30 methylimidazolyl-1-methanol in 5 ml dry benzene. Two phases are built. Stir vigorously for half an hour. Then the

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combined solvents are rotated off and a bright brown product remains. $^1\text{H-NMR}$ (CDCl_3 ; 270 MHz): 7.75 (d; 1H); 7.68 (d; 1H); 5.16 (s; 2H); 3.86 (s, 3H); 3.42 (s; 3H). $^{13}\text{C-NMR}$: 141.5; 124.7; 119.4; 34.2; 31.7 ppm.

5

1,4-bis(1-methylimidazol-2-ylmethyl)-7-ethyl-1,4,7-triazacyclononane

This ligand is produced through conversion with the 2-chloromethyl-1-methyl-imidazolhydrochloride under impact of bases. 3.32 g of the 2-chloromethyl-1-methyl-imidazolhydrochloride (20 mmol) is suspended in acetonitril whilst cooling with ice. Adding 2.77 ml triethylamine results in a brown solution. After stirring for 10 minutes a white precipitation (triethylammoniumchloride) is formed.

10 This is filtered off and washed with a minimum of acetonitril. 1.55 g Et-tacn (10 mmol) is added to the filtrate and rinsed with acetonitril. Then a further 2.9 ml triethylamine (20 mmol+5% surplus) is added and stirred for 3 hours under an argon atmosphere. Next, the reaction mixture is filtered and the solvents are drained off from the filtrate. The yellow solid product remains. Yield: 3.7 g (50%); $^1\text{H-NMR}$ (CDCl_3 - 250 MHz; 300K): 6.86 (s; 2H); 6.85 (s; 2H); 5.27 (s; 4H); 3.68 (q; 2H); 3.66 (s; 6H); 3.23 (m; 4H); 2.78 (s; 8H); 1.26 (t, 3H); $^{13}\text{C-NMR}$: 145.1; 126.1; 121.7; 51.2-55.2; 33.1; 9.6 ppm. MS (EI): m/z: 345.

15

20

25

Ligand L⁸: 1,4,7-tris(quinolin-2-ylmethyl)-1,4,7-triazacyclononane:

30 20 mmol Et-tacn (3.12 g) is dissolved in 50 ml dry THF and mixed with 8 ml triethylamine (56.8 mmol). Then 40 mmol

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quinolin-2-ylmethylbromide (8.96 g) is added, after which the solution turns brown. The reaction mixture is then stirred for 3 days. The resulting triethylammoniumbromide is filtered off and the THF is rotated off. A bright yellow
5 solid remains. The product is still polluted by approx. 2% triethylamine.

Yield: 7.7 g (70%). $^1\text{H-NMR}$ (CDCl_3 , 250 MHz; 300K): 8.01 (d; 3H); 7.98 (d; 3H); 7.73 (d; 3H); 7.66 (d; 3H); 7.64 (m; 3H); 7.47 (m; 3H); 4.02 (s; 6H); 2.96 (s; 12H). $^{13}\text{C-NMR}$:
10 160.9; 147.3; 135.9; 129.1; 128.8; 127.4; 127.2; 125.9;
121.3; 65.5; 55.8.

Ligand L⁹: 1,4-bis(N-methylamido)-7-ethyl-1,4,7-triazacyclononane:

15 This ligand is produced according to the prescription for the synthesis of amide-functionalised polyazamacrocycles of D. Parker et al (J. Chem. Soc., Perkin Trans, 2, 1990, 1425). 25 mmol 1-ethyl-1,4,7-triazacyclononan, 3.90 g, is dissolved in dried acetonitril and mixed with 50 mmol potassium carbonate, 6.9 g. After adding 50 mmol N-methyl-bromacetamide (lit W. E. Weaver and W. M. Whaley, J. Am. Chem. Soc., 69, 515, 1947), 7.60 g, the reaction mixture is heated for 24 hours under an argon atmosphere and back-flow.
20 After cooling down the potassium bromide and the remaining potassium carbonate are filtered off. After the solvent has been removed the product remains as a bright yellow solid.
25 Yield: 6.6 g (75%). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz; 300K): 8.12 (s; 2H); 3.21 (s; 4H); 2.72 (m; 12H); 2.59 (q, 2H); 1.02 (t; 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 270 MHz; 300K): 172.7; 61.5; 56.0; 55.3; 53.7; 52.7; 25.7; 12.0 ppm. MS(EI): m/z: 299.

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Ligand L¹⁰: 1,4-bis(N-isopropylamido)-7-ethyl-1,4,7-triazacyclononane:

25 mmol 1-ethyl-1,4,7-triazacyclonan, 3.90 g, is dissolved
5 in dried acetonitril and mixed with 50 mmol potassium
carbonate, 6.9 g. After adding 50 mmol N-i-
propylbromacetamide (lit W. E. Weaver and W. M. Whaley, J.
Am. Chem. Soc., 69, 515, 1947), 9.0 g, the reaction mixture
is heated for 24 hours under an argon atmosphere and back-
10 flow. After cooling down the potassium bromide and the
remaining potassium carbonate are filtered off. After the
solvent has been removed the product remains as a bright
yellow solid, analogous to the description of D. Parker et
al. (J. Chem. Soc., Perkin Trans, 2, 1990, 1425).
15 Yield: 6.2 g (70%) ¹H-NMR (CDCl₃, 400 MHz; 300K): 7.35 (d;
2H); 4.01 (sept, 2H); 3.13 (s; 4H); 2.80 (m; 4H); 2.76 (m,
4H); 2.65 (s; 4H); 2.59 (q, 2H); 1.09 (d, 12H); 0.98 (t;
3H). ¹³C-NMR (CDCl₃, 270 MHz; 300K): 172.7; 62.4; 58.3; 57.6;
55.1; 53.1; 40.8; 22.9; 11.6 ppm.

20

Experimental:

Example 1:

25 In an aqueous solution containing 10 mM carbonate buffer (pH
10) without and with 0.6 g/l NaLAS (linear alkylbenzene
sulfonate) or containing 10 mM borate buffer (pH 8) without
and with 0.6 g/l NaLAS, tomato-soya oil stained cloths were
added and kept in contact with the solution under agitation
30 for 30 minutes at 30 °C. In comparative experiments, the same

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experiments were done by addition of 10 µM complex, referred to in the table below.

After the wash, the cloths were rinsed with water and
5 subsequently dried at 30 °C and the change in colour was measured immediately after drying with a Linotype-Hell scanner (ex Linotype). The change in colour (including bleaching) is expressed as the ΔE value; a higher ΔE value means a cleaner cloth. The measured colour difference (ΔE)
10 between the washed cloth and the unwashed cloth is defined as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

15 wherein ΔL is a measure for the difference in darkness between the washed and unwashed test cloth; Δa and Δb are measures for the difference in redness and yellowness respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission
20 International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric colour terms, supplement no 2 to CIE Publication, no 15, Colormetry, Bureau Central de la CIE, Paris 1978. The results are shown below in Table 1:

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Table 1

| | pH 8 - LAS | pH 8 + LAS | pH 10 - LAS | pH 10 + LAS |
|------------|------------|------------|-------------|-------------|
| Blank | 1 | 2 | 1 | 3 |
| Compound 1 | 2 | 12 | 1 | 4 |
| Compound 2 | 2 | 14 | 3 | 8 |
| Compound 3 | 16 | 17 | 16 | 17 |
| Compound 4 | 3 | 9 | 3 | 9 |
| Compound 5 | 5 | 10 | 4 | 6 |

Example 2:

5

Bleach values expressed in ΔE (a higher value means a cleaner cloth). Stain: curry oil stain. Washed for 30 min at 30 °C, rinsed, dried and measured. In all cases 10 μM of metal complex is added to the wash liquor (except for 10 blank). The results are shown below in Table 2:

Table 2

| | pH 8 - LAS | pH 8 + LAS | pH 10 - LAS | pH 10 + LAS |
|------------|------------|------------|-------------|-------------|
| Blank | 1 | 3 | 3 | 15 |
| Compound 1 | 2 | 12 | 1 | 24 |
| Compound 2 | 2 | 14 | 3 | 32 |
| Compound 3 | 16 | 17 | 16 | 27 |
| Compound 4 | 3 | 9 | 3 | 23 |
| Compound 5 | 5 | 10 | 4 | 23 |

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CLAIMS:

1. A bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing bleaching of a substrate by the atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, wherein the ligand forms a complex of the general
5 formula (A1) :



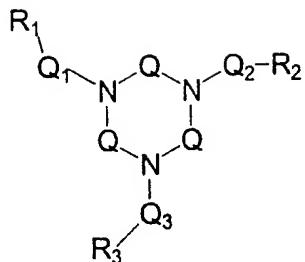
in which:

15 M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI);

X represents a coordinating species selected from any
20 mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;
a represents an integer from 1 to 10;
25 k represents an integer from 1 to 10;
n represents an integer from 1 to 10;
m represents zero or an integer from 1 to 20; and
L represents a ligand of the general formula (I), or its protonated or deprotonated analogue:

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(I)

wherein

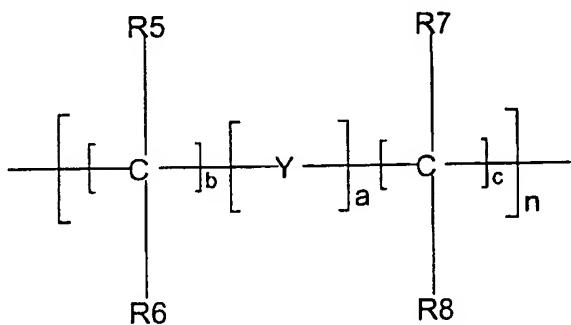
5

R_1 , R_2 , and R_3 independently represent a group selected from hydrogen, hydroxyl, halogen, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$, $-\text{R}$ and $-\text{OR}$, wherein R = alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E ;

10

Q independently represent a group selected from C_{2-3} -alkylene optionally substituted by H, benzyl or C_{1-8} -alkyl;

15 Q_1 , Q_2 and Q_3 independently represent a group of the formula:



20

wherein

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5 $\geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -
5 S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene,
heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G
is selected from hydrogen, alkyl, aryl, arylalkyl,
cycloalkyl, each except hydrogen being optionally
substituted by one or more functional groups E;

10

R5, R6, R7, R8 independently represent a group selected
from hydrogen, hydroxyl, halogen, -R and -OR, wherein R
represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl,
aryl, heteroaryl or a carbonyl derivative group, R being
15 optionally substituted by one or more functional groups E,
or R5 together with R6, or R7 together with R8, or
both, represent oxygen,

or R5 together with R7 and/or independently R6 together
with R8, or R5 together with R8 and/or independently R6
20 together with R7, represent C₁₋₆-alkylene optionally
substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I; and

E independently represents a functional group selected
from -F, -Cl, -Br, -I, -OH, -OR', -NH₂, -NHR', -N(R')₂, -
25 N(R')₃⁺, -C(O)R', -OC(O)R', -COOH, -COO⁻(Na⁺, K⁺), -COOR', -
C(O)NH₂, -C(O)NHR', -C(O)N(R')₂, heteroaryl, -R', -SR', -SH, -
P(R')₂, -P(O)(R')₂, -P(O)(OH)₂, -P(O)(OR')₂, -NO₂, -SO₃H, -SO₃⁻
(Na⁺, K⁺), -S(O)₂R', -NHC(O)R', and -N(R')C(O)R', wherein R'
represents cycloalkyl, aryl, arylalkyl, or alkyl optionally

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substituted by -F, -Cl, -Br, -I, -NH₃⁺, -SO₃H, -SO₃⁻(Na⁺, K⁺), -COOH, -COO⁻(Na⁺, K⁺), -P(O)(OH)₂, or -P(O)(O⁻(Na⁺, K⁺))₂,

provided that at least one, preferably at least two, of
5 R₁, R₂ and R₃ is a coordinating group.

2. A bleaching composition according to claim 1, wherein
the medium has a pH value in the range from pH 6 to 11,
preferably in the range from pH 8 to 10.

10

3. A bleaching composition according to claim 1 or claim
2, wherein the medium is substantially devoid of a
transition metal sequestrant.

15 4. A bleaching composition according to any of claims 1 to
3, wherein the medium further comprises a surfactant.

5. A bleaching composition according to any of claims 1 to
4, wherein the medium further comprises a builder.

20

6. A bleaching composition according to any of claims 1 to
5, wherein the composition comprises a preformed complex of
the ligand and a transition metal.

25 7. A bleaching composition according to any of claims 1 to
5, wherein the ligand is present as a free ligand that
complexes with a transition metal present in the water.

8. A bleaching composition according to any of claims 1 to
30 5, wherein the ligand is present as a free ligand that
complexes with a transition metal present in the substrate.

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9. A bleaching composition according to any of claims 1 to 5, wherein the composition comprises the ligand present as a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

5

10. A bleaching composition according to any preceding claim, wherein at least two of R₁, R₂ and R₃ independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

15

11. A bleaching composition according to any preceding claim, wherein at least two of R₁, R₂, R₃ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

12. A bleaching composition according to any preceding claim, wherein R₅, R₆, R₇, R₈ independently represent a group selected from -H, hydroxy-C₀-C₂₀-alkyl, halo-C₀-C₂₀-alkyl, nitroso, formyl-C₀-C₂₀-alkyl, carboxyl-C₀-C₂₀-alkyl and esters and salts thereof, carbamoyl-C₀-C₂₀-alkyl, sulfo-C₀-C₂₀-alkyl and esters and salts thereof, sulfamoyl-C₀-C₂₀-alkyl, amino-C₀-C₂₀-alkyl, aryl-C₀-C₂₀-alkyl, C₀-C₂₀-alkyl,

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alkoxy-C₀-C₆-alkyl, carbonyl-C₀-C₆-alkoxy, and C₀-C₂₀-alkylamide.

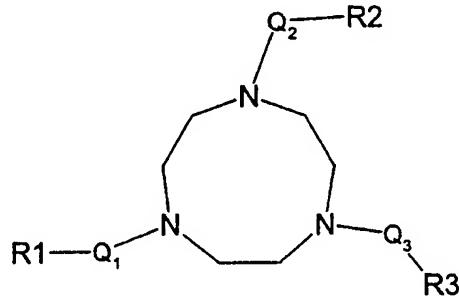
13. A bleaching composition according to any preceding
5 claim, wherein Q₁, Q₂ and Q₃ are defined such that a=b=0,
c=1,2,3 or 4 and n=1.

14. A bleaching composition according to any preceding
claim, wherein Q₁, Q₂ and Q₃ independently represent a group
10 selected from -CH₂- and -CH₂CH₂-.

15. A bleaching composition according to any preceding
claim, wherein Q represents a group selected from -CH₂CH₂-
and -CH₂CH₂CH₂-.

15

16. A bleaching composition according to any preceding
claim, wherein the ligand L is of the general formula (II):



20

(II)

17. A bleaching composition according to claim 16, wherein
R1, R2, R3 each independently represent a coordinating group
selected from carboxylate, amido, -NH-C(NH)NH₂,
25 hydroxyphenyl, an optionally substituted heterocyclic ring

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or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and
5 thiazole.

18. A bleaching composition according to claim 17, wherein R₁, R₂, R₃ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl,
10 optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

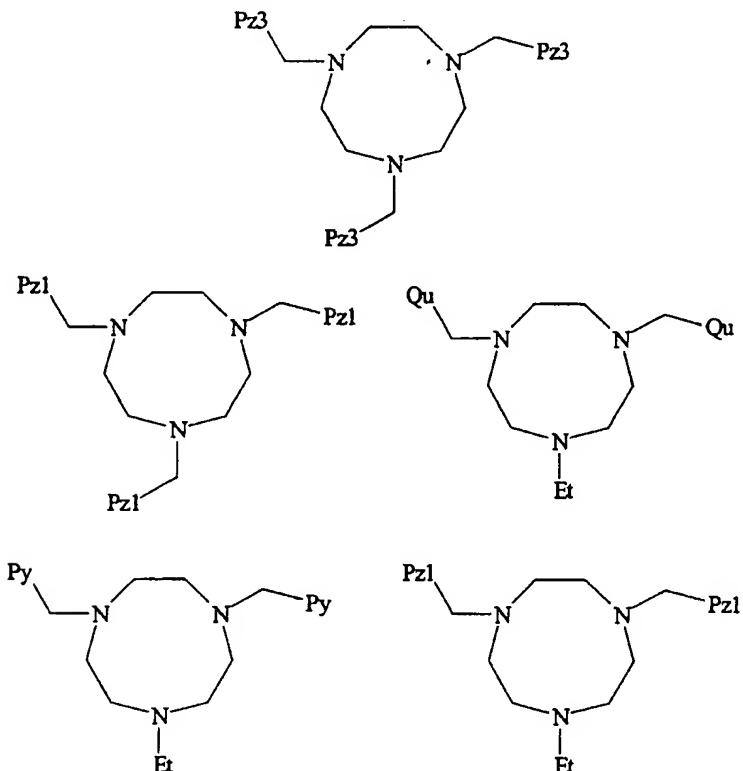
19. A bleaching composition according to claim 16, wherein
15 two of R₁, R₂, R₃ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenol, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine,
20 pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and
one of R₁, R₂, R₃ represents a group selected from hydrogen, C₁₋₂₀ optionally substituted alkyl, C₁₋₂₀ optionally substituted arylalkyl, aryl, and C₁₋₂₀ optionally substituted NR₃⁺ (wherein R=C₁₋₈-alkyl).

20. A bleaching composition according to claim 19, wherein
two of R₁, R₂, R₃ each independently represent a
30 coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl,

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optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and one of R1, R2, R3 represents a group selected from hydrogen, C₁₋₁₀ optionally substituted alkyl, C₁₋₅-furanyl, C₁₋₅ 5 optionally substituted benzylalkyl, benzyl, C₁₋₅ optionally substituted alkoxy, and C₁₋₂₀ optionally substituted N⁺Me₃.

21. A bleaching composition according to claim 16, wherein L represents a ligand selected from:



10

wherein -Et represents ethyl, -Py represents pyridin-2-yl, Pz3 represents pyrazol-3-yl, Pz1 represents pyrazol-1-yl, and Qu represents quinolin-2-yl.

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22. A bleaching composition according to any preceding claim, wherein the composition comprises a mixture of the ligand L and a metal salt MX_n in which n=1-5, preferably 1-3.

5 23. A method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen, wherein the ligand is as defined in any of claims 1 to 21.

10

24. A method according to claim 23, wherein the majority of the bleaching species in the medium (on an equivalent weight basis) is derived from the atmospheric oxygen.

15 25. A method according to claim 23 or claim 24, wherein the medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

20 26. A method according to any preceding claim, wherein the aqueous medium is agitated.

27. A method according to any of claims 23 to 26, wherein the medium is as defined in any of claims 2 to 5.

25 28. Use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, the complex catalysing bleaching of the substrate by the atmospheric oxygen wherein the ligand is as defined in any of claims 1 to 21.

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29. A method of treating a textile by contacting the textile with a ligand which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment,
5 wherein the ligand is as defined in any of claims 1 to 21.

30. A method according to claim 29, wherein the treatment comprises contacting the textile with the ligand in dry form.

10

31. A method according to claim 30, wherein the treatment comprises contacting the textile with a liquor containing the ligand and then drying.

15 32. A method according to claim 31, wherein the liquor is an aqueous liquor.

33. A method according to claim 32, wherein the liquor is a spray-on fabric treatment fluid.

20

34. A method according to claim 32, wherein the liquor is a wash liquor for laundry cleaning.

25 35. A method according to claim 31, wherein the liquor is a non-aqueous liquor.

36. A method according to claim 35, wherein the liquor is a dry cleaning fluid.

30 37. A method according to claim 35, wherein the liquor is a spray-on aerosol fluid.

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38. A method according to any of claims 31 to 37, wherein the liquor is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

5

39. A dry textile having a ligand as defined in any of claims 1 to 21 applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/08075

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D3/39 D06L3/02 C07D255/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D D06L C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-------------------------------------|
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/08075

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